Mixed stereochemistry \((Q_1 + D_{02})\) was proposed for Ni(II) complexes on the basis of magnetic moment data. The electronic spectra of these complexes show bands at about 8000, 14,849 and 235 kK characteristic of an octahedral geometry. The weak intensity band characteristic of Ni(II) in square planar environment appears to have submerged in the strong intensity 42 band of octahedrally coordinated Ni(II).

The 2222 and 1587 kK bands in the spectra of Cu(IPTSC-H)Cl and Cu(IPTSC-2H) indicate square planar and highly distorted octahedral geometries respectively for the two complexes.

\[
R = NH_{2}NH_{2}CSNHPh
\]

A negative shift in \(v(N-H)\) bands in all the complexes except in the case of VO(IPTSC-2H), as compared with the solution spectrum (in acetonitrile) of the ligand indicates the involvement of at least one of the \(\geq \) bands of the ligands in bonding. The amide-I band suffers a negative shift in the spectra of the adducts as compared with the free ligand and disappears in the spectra of condensation compounds, indicating the involvement of the \(\geq \) group in the latter complexes as compared with the solution spectrum (in acetonitrile) of the ligand indicates the involvement of at least one of the \(\geq \) bands of the ligands in bonding. This is in accord with the carbonyl oxygen in the adducts and carbonyl oxygen as well as pyridine nitrogen in the latter 10.

The \(v(C=O)\) band of the ligand indicates the involvement of at least one of the \(\geq \) bands of the ligands in bonding. This is in accord with the carbonyl oxygen in the adducts and carbonyl oxygen as well as pyridine nitrogen in the latter 10.

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The positive shift in the \(v(N-N)\) mode \(v(\geq)\) is either very weak or disappears completely in the spectra of VO(IPTSC) complexes compared with the solution spectrum of the ligand in acetonitrile.

One of the authors (R.B.S.Y.) is thankful to CSIR, New Delhi, for financial assistance.

References


Synthesis of Substituted Dimethylformamidyl Te(II) & Se(II) Chlorides

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Received 3 March 1976; accepted 3 June 1976

Substituted dimethylformamidyl tellurium(IV) chloride \([TeCl_3CON(CH_3)_2DMF]\) and selenium(IV) chloride, \([SeCl_3CON(CH_3)_2]\) have been prepared by the reaction of TeCl_4 and SeCl_4 with dimethylformamidyl sodium. The compounds have been characterized on the basis of elemental analyses, molar conductance and IR spectral data.

In continuation of our earlier report on the preparation of alkali metal dimethylformamidyls, we now report the preparation and characterization of substituted dimethylformamidyl compounds, \([TeCl_3CON(CH_3)_2DMF]\) and \([SeCl_3CON(CH_3)_2]\) of Te(IV) and Se(IV) chlorides.

Preparation of \([TeCl_3CON(CH_3)_2DMF]\) (I) — On stirring an equimolar mixture of TeCl_4 and NaCON \((CH_3)_2\) in CCl_4 for 7-8 hr, a dark brown voluminous solid separated which was filtered, washed with
ccl₄ and dried. Sodium chloride formed and any unreacted NaCON(CH₃)₂ were removed by treating the solid with DMF. The DMF solution on evaporation under reduced pressure yielded a mustard coloured powder analysing for TeCl₂CON(CH₃)₀. Insoluble in CCl₄ benzene and slightly soluble in methylene chloride, nitrobenzene and nitromethane.

The suspension of I in CCl₄ on refluxing with quinoline (Q) yielded a white solid, TeCl₂CON(CH₃)₀.Q, insoluble in CCl₄ benzene and slightly soluble in methylene chloride, nitrobenzene and nitromethane.

Preparation of SeCl₂CON(CH₃)₁.

Preparation of SeCl₂CON(CH₃)₁. (II) - It was prepared in a manner analogous to compound I. However, the separation of NaCl and unreacted NaCON(CH₃)₂ could not be affected by treatment with DMF, as the compound disproportionated to give elemental Se. The compound dissolved in methylene chloride on prolonged stirring and insoluble NaCl and NaCON(CH₃)₂ were removed by filtration. The solution on evaporation under reduced pressure yielded a yellow semi-solid, SeCl₂CON(CH₃)₁. This compound is soluble in methylene chloride and slightly soluble in CCl₄, nitrobenzene and nitromethane.

The analytical results are given in Table 1. All these compounds are highly sensitive to moisture.

Solvolytic reactions of metal halides do not take place in DMF due to the very low acidity of the medium. These compounds are highly sensitive to moisture.

Preparation of SeCl₂CON(CH₃)₁. (II) - It was prepared in a manner analogous to compound I. However, the separation of NaCl and unreacted NaCON(CH₃)₂ could not be affected by treatment with DMF, as the compound disproportionated to give elemental Se. The compound dissolved in methylene chloride on prolonged stirring and insoluble NaCl and NaCON(CH₃)₂ were removed by filtration. The solution on evaporation under reduced pressure yielded a yellow semi-solid, SeCl₂CON(CH₃)₁. This compound is soluble in methylene chloride and slightly soluble in CCl₄, nitrobenzene and nitromethane.

Table 1 - Analytical Data of the Compounds

<table>
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<tr>
<th>M</th>
<th>Cl</th>
<th>C</th>
<th>H</th>
<th>N</th>
</tr>
</thead>
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<tr>
<td>TeCl₂CON(CH₃)₀, DMF</td>
<td>100-102</td>
<td>17-9</td>
<td>3-3</td>
<td>7-8</td>
</tr>
<tr>
<td></td>
<td>(33-6)</td>
<td>28-1</td>
<td>19-0</td>
<td>3-4</td>
</tr>
<tr>
<td>TeCl₂CON(CH₃)₀, Q</td>
<td>195</td>
<td>31-8</td>
<td>2-8</td>
<td>6-0</td>
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<tr>
<td></td>
<td>(29-2)</td>
<td>24-4</td>
<td>33-2</td>
<td>3-0</td>
</tr>
<tr>
<td>SeCl₂CON(CH₃)₁</td>
<td>29-6</td>
<td>39-5</td>
<td>14-4</td>
<td>2-6</td>
</tr>
<tr>
<td></td>
<td>(30-7)</td>
<td>41-3</td>
<td>14-0</td>
<td>2-3</td>
</tr>
</tbody>
</table>

Molar conductivities of the millimolar solutions of compound I (2.3 ohm⁻¹ cm² mol⁻¹) and of its quinoline adduct (2.2 ohm⁻¹ cm² mol⁻¹) in nitrobenzene indicate that they behave as 1:1 electrolytes. The other possibility is the ionization of solvated formamidyl anion (Eq. 2).

The existence of this anion in the form of its alkali metal salts has been earlier proposed by Bredereck et al.². The IR bands of selenium compound, (II) could not be recorded as it will not form mull with nujol and it reacted with KBr and CsI plates.

Thermal behaviour of I as well as of its quinoline adduct shows that these decompose finally to be TeO₂ through the formation of some unstable intermediates. From the total loss in weight the composition of the compound was checked. The composition of the intermediate products could not be ascertained.

References

Compounds of Thallium(III) Chloride with Some Lewis Acids

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A number of adducts of thallium(III) chloride with Lewis acids have been isolated. On the basis of conductance, molecular weight and IR data, the adducts with phosphorus pentachloride, iodine trichloride and tetrachlorides of selenium and tellurium have been formulated as PCI₃·TlCl₃, ICl₃·TlCl₃ and MCl₄·TlCl₃ respectively; but in the case of trichlorides of phosphorus, arsenic and antimony, the adducts obtained have been characterized as halogen-bridged four-coordinated Ti(III) compounds.

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